

UNCLASSIFIED

Defense Technical Information Center  
Compilation Part Notice

ADP011804

TITLE: Chemical Processing of Nanostructured Coatings

DISTRIBUTION: Approved for public release, distribution unlimited

This paper is part of the following report:

TITLE: NATO Advanced Research Workshop on Nanostructured Films and Coatings. Series 3. High Technology - Volume 78

To order the complete compilation report, use: ADA399041

The component part is provided here to allow users access to individually authored sections of proceedings, annals, symposia, etc. However, the component should be considered within the context of the overall compilation report and not as a stand-alone technical report.

The following component part numbers comprise the compilation report:

ADP011800 thru ADP011832

UNCLASSIFIED

## CHEMICAL PROCESSING OF NANOSTRUCTURED COATINGS

LYNN K. KURIHARA  
*Code 6354, Multifunctional Materials Branch*  
*Naval Research Laboratory*  
*Washington DC 20375 USA*  
*Email: kurihara@anvil.nrl.navy.mil*  
*Also at*  
*Potomac Research International*  
*Fairfax VA 22030 USA*

### 1. Introduction

Nanostructured materials, often characterized by a physical dimension of 1-100 nm (such as grain size) and significant amount of surfaces and interfaces, have been attracting much interest because of their demonstrated or anticipated unique properties compared to the conventional materials (1-3). Nanophase coatings can enhance the surface properties and yet retain the bulk properties of the coarse grained substrate material.

Nanostructured films can be prepared by evaporative technologies, glow discharge, gas-phase processes and liquid phase chemical routes. There has been a growing interest in chemical routes because of the many advantages it has over the other technologies. The advantages of chemical routes include: the ability to control the chemical composition, the particle size distribution, agglomerate size distribution, particle morphology, porosity, and the advantages of low temperature processing and cost-effective bulk quantity production. Examples of chemical routes used for preparing nanostructured coatings are: sol-gel processing, polyol, electroplating, electrodeless plating, electrophoretic deposition and electrolytic anodization. The scope of this chapter will be restricted to sol-gel processing and polyol chemistry.

### 2. Sol-Gel Processing of Nanostructured Coatings

Sol-gel processing involves the synthesis of an inorganic network by chemical reactions in a solution at low temperature (4). The solution or sol is a dispersion of solid particles in a liquid, and the gel is the result of the formation of a three dimensional network which spans the entire solution volume. The reaction usually takes place at room temperature. The traditional precursors for sol-gel reactions have been metal alkoxides. Although, a variety of metal precursors can be used, such as metal nitrate or other metal-organic compounds. Sol-gel is a versatile technique. Using sol-gel techniques, many types of materials may be made. They include aerogels, xerogels, powders, glasses, coatings, fibers, whiskers, monoliths, hollow spheres and foams. Depending on the synthesis conditions, coatings, porous solids, powders, fibers, bulk materials may be prepared. From solution, coatings may be applied to a substrate, or fibers may be drawn if the viscosity of the sol is high enough. If the sol is allowed to start to gel, a porous solid or a powder can be formed from the gel. The porous solid or nanopowder can also be used as a starting material for some coating techniques.

There are many types of sol-gel coatings in the literature ranging from IR imaging to anti-scratch to smart windows and waveguides. Uhlmann and Towee have taken a survey of the sol-gel community (5) and found that it was considered that coatings were the most important present products using sol-gel processing, and it was also reported that functional coatings would be considered the most important commercial product in ten years. The reasons behind these choices were that, with sol-gel, coatings could be obtained with compositions that are not obtainable by other means; sol-gel provides the ability to do integrated multilayers at a lower cost than vacuum techniques and sol-gel can easily be combined with other preparative systems. Painting, spinning, dipping, spraying, electrophoresis (6), and ultrasonic pulverization (7) may be employed to put down coatings and films from sol-gel solutions. The last two techniques have

recently been getting more attention, as they can be used to prepare thicker coatings. The most common deposition techniques are that of spinning or dipping. A drawback of these techniques is that they are generally limited to the deposition of axially or radially symmetric substances. Sol-gel processing is especially adaptable for coating formation. Films and coatings represent the earliest commercial use of sol-gel processing. Sol-gel techniques offer the following advantages. Controlling the pore volume, pore size and the surface area can control microstructure; that is, the film properties can be tailored. It is also possible to obtain compositions that are not available by other routes such as gas condensation. Thin films use very small quantities of raw materials and can be processed quickly, and very large and irregularly shaped surfaces can be coated. Dense pinhole free layers can be prepared at low temperatures using sol-gel processing. Porous films can be prepared by changing the reaction conditions. This approach is particularly useful to obtain homogeneous multicomponent coatings. To avoid cracking caused by large capillary stresses during evaporation of solvent in the drying process, either slow evaporation (slow process) or supercritical drying (fast process) is used. As-deposited oxide coatings are typically amorphous. Thermal and thermochemical post-synthesis treatment can be carried out to obtain nanostructured oxide, carbide or nitride coatings. Hybrid coatings can be fabricated by doping the sol with material of a different phase, followed by gelation and densification. Because of the large capillary stress during solvent evaporation that can cause cracking, sol-gel process has been traditionally used for preparing thin films and coatings. Generally, the film thickness is less than a micron. To prepare thick coatings, the problems of shrinkage and cracking and the limitation of coating thickness can be mitigated by increasing particle loading in sol-gel process (8-10). This approach involved dispersing large ceramic powders in sol-gel solution, and the mixture was applied onto the substrate by various techniques such as dipping and spraying. Coatings with thickness up to 200  $\mu\text{m}$  were fabricated. The sol-gel film formed strong bonds to both oxide powders and substrates by interaction with functionalized surface hydroxyl groups on the oxide powders and the oxide layer of substrates. The strong bond reduced cracking. The shrinkage problem associated with conventional sol-gel approach was minimized due to the high loading of ceramic powders. One way to prepare thicker coatings is to add powders into the sol. This helps to reduce the capillary stresses associated with drying. Chen and coworkers (9) have prepared thick coatings by adding nanosized boehmite, alumina, zirconia or silicon carbide into an inorganic-organic hybrid matrix. A two dimensional sol-gel process was also used to fabricate thick films of titania (11). In this process, the traditional sol-gel hydrolysis and condensation reactions took place at an air-water interface. The gel films formed could then be deposited onto substrates using Langmuir Blodgett techniques.

The ability to process at room temperature has also opened up the biomaterials aspect of sol-gel chemistry. Proteins and enzymes can be encapsulated in silica glass (12), while still retaining their activity. Sol-gel coatings (13,14) of hydroxyapatite should also aid in the implantation of artificial bones or joints with of the surrounding tissue.

As previously mentioned, the processing of sol-gel coatings can be controlled to form porous coatings. The porosity may be used as a template or reaction site for other materials or chemical reactions to take place or this porosity may be used to change physical properties. The real advantage of sol-gel processing is that this porosity can be controlled. Films with pore sizes below 10 nm and patterned (15,16) can be prepared. These pores can be filled by surface adsorption from aqueous solutions of the desired cations. The doping time and temperature, and solution pH can control this doping process.

Composite coatings can be prepared by doping other materials into a porous matrix. Metal clusters of Ag, Cu and Ag-Cu have been prepared in silica films (17). These metal clusters have enhanced third order nonlinear susceptibility, and these properties can be tuned by controlling the cluster size. The nanocluster size can be controlled by temperature and annealing atmosphere in the processing of these materials. Conducting polymers such as polyaniline can also be entrapped in the porous silica coating (18). This hybrid system improves the conductivity and stability of the conducting polymer.

Ferroelectric films have many potential applications in a variety of solid state devices such as RAM, sensors, and actuators. Sol-gel preparation of films of ferroelectric materials is generating a lot of interest because of the ease of integrating the films into microelectronics manufacturing processes. Adding nanoporosity in ferroelectric coatings is one way to change the dielectric constant in a coating while keeping the thermal and mechanical properties of the coatings. Sol-gel processing can be used to prepare polymeric organic-inorganic hybrids with controlled morphologies. Using a thermally labile macromolecule template for the vitrification of a silsequioxane precursor allows this to be achieved (19). The organic moiety can be removed by heat treatment to leave a nanoporous structure. The pore size is controlled by the template polymerization. However, it may not be advantages to add a nanoporous coating to a device.  $\text{Pb}(\text{Zr}_{.53}\text{Ti}_{.47})\text{TiO}_3$  thin films with crystallite sizes of 23 nm at 800°C can be prepared

by using the methoxyethoxides of the starting elements (20). It was found that the annealing temperature is the important parameter. However, defects or uncontrolled porosity can lead to short circuits (21). It was determined that having a film with low porosity and nanosized pores can decrease the number of short circuits. This can be done by control the hydrolysis reactions in the precursor gel by regulating the pH and the water to alkoxide ratio. Lead titanate films with crystallite size of 160 nm at 800°C had a  $\epsilon = 190$  and a  $\tan \delta$  of 8%. Sol-gel processing has also been used to prepare fine-grained (<70 nm) polycrystalline barium titanate films (22-24). These films generally have the cubic perovskite structure instead of the ferroelectric tetragonal structure. It was noted that the dielectric properties of barium titanate films also decreased as the grain size decreased. A detailed TEM (24) study of nanocrystalline barium titanate films showed that the microstructure was independent of variations in processing parameters, such as: amount of water, precursor type, solvent, and pH. In-situ TEM studies showed a intermediate carbonate phase is formed around 600°C that decomposes to leave nanoporosity in the final film at higher temperatures and the nanocrystalline barium titanate is formed by nucleation on this intermediate phase.

## 2.1 Sol-gel processing of thermal barrier coatings

Thermal barrier coatings (TBC) generally consist of zirconia ( $\text{ZrO}_2$ ) or yttria-stabilized zirconia (YSZ) and more recently alumina-stabilized zirconia (ASZ).  $\text{ZrO}_2$  is of particular interest for TBCs because of its chemical and temperature stability, hardness and low thermal conductivity. However, pure zirconia has a very serious drawback, related to high temperature phase stability. That is, depending on the temperature, that  $\text{ZrO}_2$  has three distinct crystal structures. In the past, different approaches have been tried to stabilize the high temperature phase of zirconia. The most common method for this phase stabilization is alloying zirconia with yttria. However, yttria is severely attacked by hot corrosion and mechanical failures of the TBC are caused by scale between the  $\text{Al}_2\text{O}_3$  scale on the bond coat and the YSZ. One advantage of using alumina as the stabilizer instead of yttria would be that the mismatch between the TBC and the bondcoat would be removed, besides not suffering from the hot corrosion problem associated with YSZ.

Sol-gel routes have been used to prepare alumina-stabilized zirconia (25,26). Nanophase alumina stabilized zirconia should show increased resistance to cracking due to better thermal-mechanical matching with the substrate material, and should have enhanced mechanical properties, such as increased fracture toughness and higher modulus of elasticity, as well as increased resistance to oxidation and hot corrosion attack.

Coatings of ASZ were prepared on stainless steel 304 coupons by dip coating. X-ray diffraction (XRD) and scanning electron microscopy (SEM) were used to characterize the samples. The coatings prepared on the SS substrates were transparent and adherent as deposited. Figure 1 shows the results of 10% $\text{Al}_2\text{O}_3$ -90% $\text{ZrO}_2$  after a heat treatment at 1200°C for 2 hours. Only the tetragonal phase of  $\text{ZrO}_2$  and the stainless steel substrate peaks are present. The average crystallite size from XRD line broadening was found to be 32 nm.

In an attempt to prepare thick coatings of zirconia, zirconia sols were loaded with solid particles of either a sol-gel-derived boehmite (amorphous) and a commercially available nanocrystalline alumina. Preliminary results are given in Table I. It was found that the amorphous sol-gel derived boehmite helped to stabilize the tetragonal phase of zirconia as well as aiding in the production of a thicker coating. Further research is being done to optimize solids loading as well as coating thickness (10).

Table I. Effects of solids loadings on zirconia phase.

Solid Dopant	Amount (vol%)	Phase of $\text{ZrO}_2$ After 1200°C/2hr	Ave. crystallite size (nm)	Coating thickness (nm)
None	None	Monoclinic	22	40
n-SG $\text{AlOOH}$	1	Monoclinic	23	46
n-SG $\text{AlOOH}$	20	Tetragonal	29	525
		Monoclinic	35	
		Alpha alumina	11	
37 nm $\text{Al}_2\text{O}_3$	20	Monoclinic	140	876
		Alpha alumina	38	

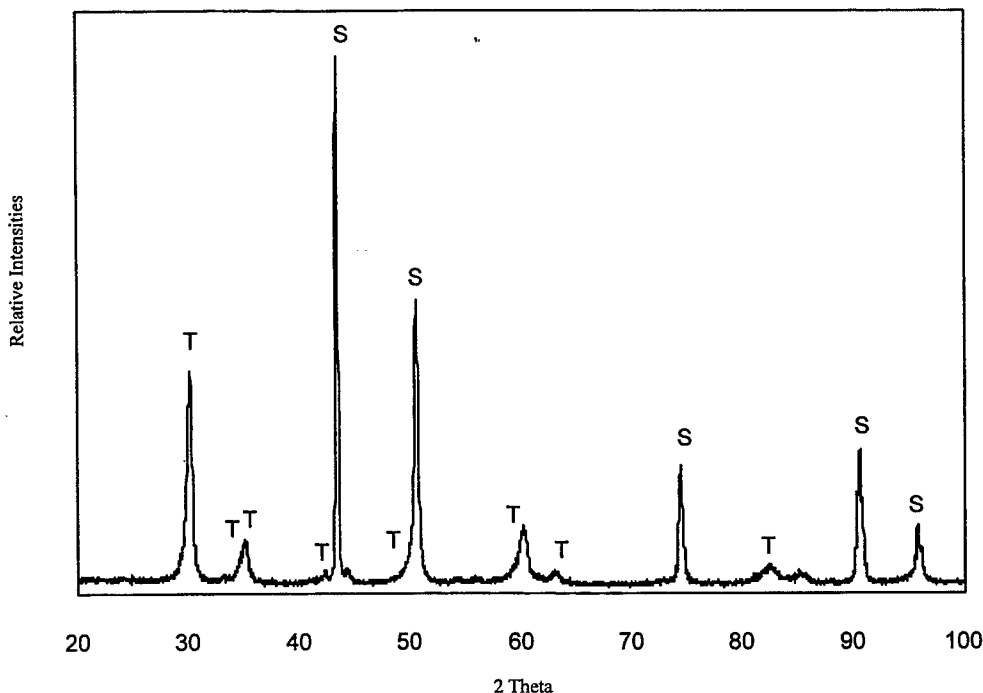


Figure 1. X-ray diffraction pattern of 10%Al<sub>2</sub>O<sub>3</sub>-90%ZrO<sub>2</sub>. The tetragonal peaks of zirconia are marked as well as the stainless steel substrate peaks.

### 3. Polyol Method for Preparing Nanocrystalline Metallic Coatings

Another chemical route for preparing nanostructured coatings is the polyol method. In this method, the metal precursors are first suspended in ethylene glycol. As the temperature is increased toward the reflux temperature, a soluble species is formed that is then reduced by the ethylene glycol. This method can be used to prepare nanocrystalline powders, coatings, and composite materials (27-30).

Nanocrystalline films of copper on AlN were prepared using the polyol method (30,31). Grazing incidence X-ray scattering (GIXS) techniques and small angle scattering techniques were used to determine the evolution of structure as a function of depth as well as the presence of nanometer size structures in the films. Copper is deposited on AlN substrates suspended inside the refluxing solution for a specific amount of time. The substrate is either placed horizontally (H) or vertically (V) with respect to the bottom of the solution flask. The resulting films have thickness that range between 2 and 4 microns.

In order to investigate the nature and origin of the textured region of the coatings, GIXS was used to look at the in-plane structure of the 20 and 30-minute films. Figures 2a-d show the GIXS contour scan of the Cu (200) on 20 and 30 minute samples grown in both a horizontal (Figure 2a, c) as well as vertical (Figures 2 b, d) substrate respectively. The scans consist of a number of peaks, whose d-spacings correspond to strains ranging between +0.1% to -0.6%. Figure 2 also shows that the intensity and location of the different peaks depend on the azimuthal orientation of the sample with respect to the incoming beam.

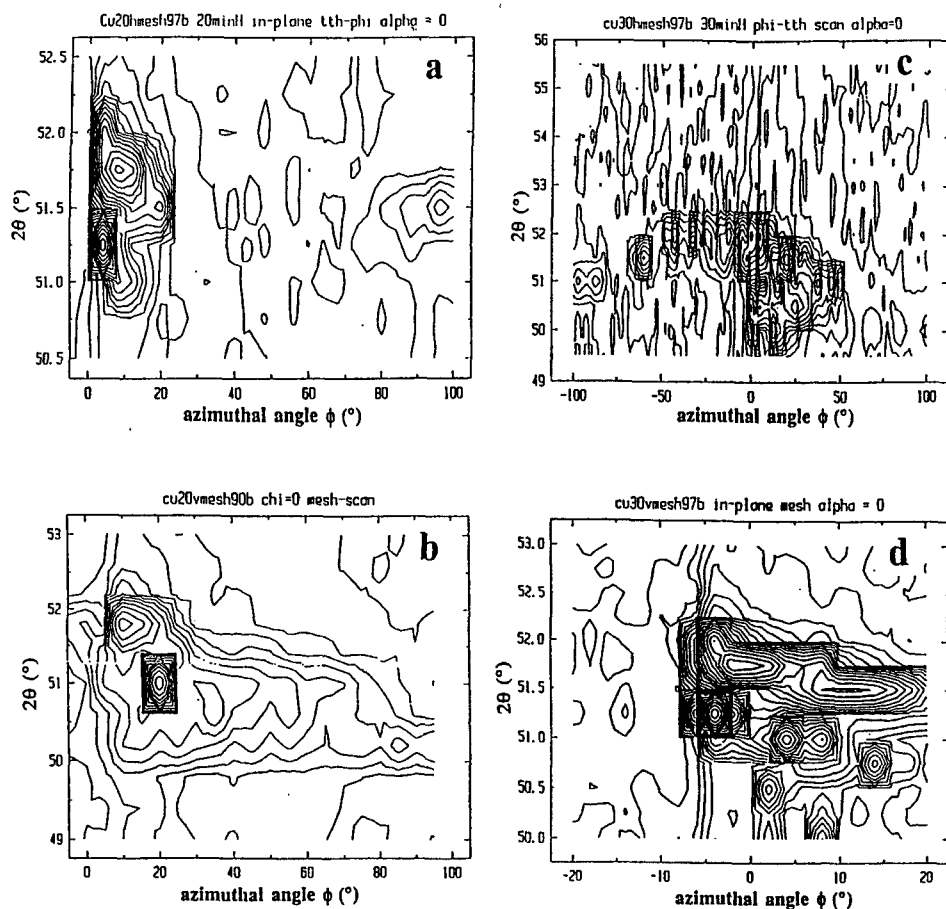


Figure 2. In plane  $2\theta$ - $\phi$  contour maps of the Cu (200) at different deposition times and substrate orientations: a. 20 minute H; b. 20 minute V; c. 30 minute H; d. 30 minute V.

The azimuthal distribution varies both as a function of metallization time as well as substrate orientation. The 20-minute H sample has an azimuthal distribution of approximately  $20^\circ$ , whereas this distribution is  $80^\circ$  in the 20 minute V sample. This suggests that the horizontally prepared sample have in-plane texturing (a preferred azimuthal/stress orientation). This orientation becomes less evident as the metallization time increases, as seen on the 30-minute samples (Figures 2c-d). The 30-minute samples show a broad azimuthal distribution for both H samples and for the interior regions of the V samples. In-situ experiments are currently underway to elucidate film growth (32).

#### 4. Summary

Chemical routes offer many advantages for processing nanostructured coatings. By controlling the synthetic conditions, the microstructure, composition and properties of the coatings can be tuned. Sol-gel techniques were used to prepare alumina-stabilized zirconia for thermal barrier applications and the polyol method was used to prepare nanocrystalline copper coatings on AlN.

#### 5. Acknowledgements

The support of NRL core program on Nanoscale Hybrid Coatings and the ONR Affordability Initiative program on Nanostructured Coatings is acknowledged. The author would like to thank Dr. Luz Martinez-Miranda and Dr. David Lewis III for useful discussions in the course of writing this chapter.

#### References

1. Muhammed, M. and Rao, K. V. (Eds) (1999) *Proceedings of Nano98, Nanostructured Materials*, **12**.
2. Chow, G.M. and Noskova, N. I. (Eds) (1998) *Nanostructured Materials, Science and Technology*, Kluwer Academic Publishers, Dordrecht.
3. Edelstein, A. S. and Cammarata, R. C. (Eds) (1996) *Nanomaterials: Synthesis, Properties and Applications*, Institute of Physics Publishing, Bristol and Philadelphia.
4. Brinker, C. J., Hurd, A. J., Schunk, P. R., Frye, G. C., and Ashley, C.S. (1992) Review of sol-gel film formation, *Journal of Noncrystalline Solids*, **147 & 148**, 424-436.
5. Uhlmann, D. R. and Towe, G. (1998) Sol-gel science and Technology: Current State and Future Prospects, *Journal of Sol-Gel Science and Technology*, **13**, 153-162.
6. Nishinari, H., Tatsumisago, M., and Minami, T. (1996) Heat treatment effect of dispersed particles of thick silica films by using electrophoretic sol-gel deposition, *Journal of Material Science*, **31**, 6529-6533.
7. Marage, P., Langlet, M., Joubert, J. C. (1994) A new route for the deposition of SiO<sub>2</sub> sol-gel coatings, *Thin Solid Films*, **238**, 218-227.
8. Barrow, D. A., Pertoff, T.E., and Sayer, M. (1997) Thick ceramic coatings using sol-gel based ceramic -ceramic 0-3 composite, *Surface and Coating Technology*, **76-77**, 113-118.
9. Chen, Y., Jin L and Xu Y (1998) Sol-gel processing of organic- inorganic nanocomposite protective coating, *Journal of Sol-Gel Science and Technology*, **13**, 735-738.
10. Kurihara, L. K. (1999) unpublished results.
11. Moriguchi, I., Maeda, H., Teraoka, Y., and Kagawa, S. (1997) Preparation of a TiO<sub>2</sub> nanoparticulate film using a two dimensional sol-gel process. *Chemistry of Materials*, **9**, 113-118.
12. Lan, E.H., Bakul, C. D., Fukuto, J. M., Dunn, B., Zink, J. I., and Valentine, J. S., (1999) Synthesis of sol-gel encapsulated heme proteins with chemical sensing properties, *Journal of Materials Chemistry*, **9**, 45-53.
13. Haddow, D. B., Vanes, P. F., Van Noort, R (1998) Sol-gel derived calcium phosphate coatings for biomedical applications, *Journal of Sol-Gel Science and Technology*, **13**, 261-65.
14. Lolpatin, C. M. Pizziloni, V., Alford, T. L., and Lawsaon, T (1998) Hydroxyapatite powders and thin films prepared by sol-gel techniques, *Thin Solid Films*, **326**, 227-232.
15. McCarthy O. and Yeatman, E. M. (1998) Control of dopant adsorption from aqueous solution into nonporous sol-gel films, *Journal of Sol-Gel Science and Technology*, **13**, 579-584.
16. McCarthy O. and Yeatman, E. M. (1997) Selected area doping of porous sol-gel films for integrated optics. *Optics Letters*, **22**, 1864-1872.
17. De, G. (1998) Sol-gel synthesis of metal nanocluster-silica composite films, *Journal of Sol-Gel Science and Technology*, **11**, 289-298.
18. Hori, T., Kuramoto, N., Tagaya, H. Karase, M., Kadokawa, J-I. And Chiba, K. (1999) Preparation of conducting films composed of polyaniline and metal oxide by sol-gel method, *Journal of Materials Research*, **14**, 5-7.
19. Hedrich, J. L, Miller, R. D., Hawker, C. J., Carter, K. R., Volksen, W., Yoon, D. Y., and Trollsas, M. (1998) Templating Nanoporosity in thin film dielectric insulators, *Advanced Materials*, **10**, 1045-1053.
20. Ontalu, V., Cabianii, C., Vasilire, F., Parlog, C. (1996) Crystallization behavior and phase coexistence at morphotropic phase boundaries in PZT thin films prepared by sol-gel processing. *Journal of Materials Science*, **31**, 3639-3642.
21. Saegusa, K., (1997) Effect of preparation conditions on short circuits in sol -gel -derived lead titanate thin films, *Journal of Materials Science*, **32**, 5961-68.
22. Yamanashi, A., Tanaka, K. Nagatomo, T. and Omoto, O (1993) BaTiO<sub>3</sub> films on silicon -on-insulator structure, *Japanese Journal of Applied Physics. Part 1*, **32**[9B] 4179-81.
23. Xu, Z, Chae, H. K., Frey, M. H. and Payne, D. A., 1991, "Chemical Processing and Properties of Nanocrystalline BaTiO<sub>3</sub>," pp. 339-44 in *Better Ceramics Through Chemistry V*, Proceedings of the Materials Research Society Symposium, Vol. 271 (San Francisco CA 1992) M. H. Hampden-Smith, W. G. Klemperer and C. J. Brinker, MRS Pittsburgh.
24. Gust, M. C., Evans, N. D., Momoda, L. A., McCartney, M. L. (1997) In-situ transmission electron microscopy crystallization studies of sol-gel derived barium titanate, *Journal of the American Ceramic Society*, **80**, 2828-2836.
25. Kuo, J., and Bourell, D. L. (1997) Structural evolution during calcination of sol-gel synthesized alumina and alumina-8 vol% zirconia composite. *Journal of Materials Science*, **32**, 2687-2692.

26. Paterson, M. J., and Ben-Nissan, B. (1996) Multilayer sol-gel zirconia coatings on 316 stainless steel, *Surface and Coatings Technology*, **86-87**, 153-158.
27. Kurihara, L. K., Chow, G.M., and Shoen, P. E. (1995) Nanocrystalline metallic powders and films produced by the polyol method, *Nanostructured Materials*, **5**, 607-613.
28. Chow, G. M., Schoen, P.E. and Kurihara, L. K. (June 1, 1998) Nanostructured metallic powders and films via a alcoholic solvent process, US Patent 5,759,230.
29. Kurihara, L. K. and Everett, R. K., (1999) unpublished results.
30. Chow, GM, Kurihara, L. K., Ma, D, Fen, C. R., Schoen, P. E. and Martinez-Miranda, L. J. (1997) Alternative approach to electroless Cu metallization of AlN by a nonaqueous polyol process, *Applied Physics Letters*, **70**, 2315-2317.
31. Martinez-Miranda, L. J., Li, Y., Chow, G. M., and Kurihara, L. K. (1999) A depth profile study of the structure and strain distribution in chemically grown Cu films on AlN, *NanoStructured Materials*, **12**, 653-657.
32. Martinez-Miranda, L. J., and Kurihara, L. K., unpublished results.